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Introduction

Synthesis and characterization of cadmium sulfide nanocrystals in the presence of a new sulfur source *via* a simple solvothermal method⁺

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CdS nanocrystals were successfully prepared using solvothermal strategies that employed Cd(NO₃)₂·4H₂O and a new sulfurising agent from the class of thio Schiff-bases as starting materials, and propylene glycol (PG) as the solvent. X-ray diffraction (XRD) patterns and transmission electron microscopy (TEM) images show that the synthesized CdS nanostructures have hexagonal and cubic structures with a diameter of about 12 nm. The formation of CdS nanoparticles and their structure, morphology and elemental composition were studied by means of FT-IR, XRD, SEM, HR-TEM and EDAX. The optical properties of the products were characterized by optical absorption spectroscopy. Based on the results of the experiments, it was found that the reaction temperature, duration and the solvent play significant roles in the formation of the CdS nanoparticles. The initiative of this work is the application of a new thio Schiff-base (2-(benzylidene amino) benzenethiol ($C_{13}H_{11}NS$)) as a complexing and sulfurising agent for the synthesis of CdS nanostructures. A possible formation mechanism of the nanoparticles is discussed.

Among the chalcogenide compounds belonging to the II-VI family, cadmium sulfide has received much attention due to the fact that it has a wide band gap of 2.42 eV at room temperature and it exhibits excellent properties for various optoelectronic applications within the visible range of the electromagnetic spectrum.^{1,2} Therefore, CdS has a key role in photoluminescence devices and solar cells.³⁻⁶ Among nanomaterials with various dimensional structures, the study and preparation of one dimensional (1D) nanostructures such as nanorods, nanowires and nanotubes as an original base for many novel functional materials have commonly received much attention from a number of researchers owing to their distinct properties and applications in nanodevices.7 1D CdS has been prepared using various methods, such as DC electrochemical deposition,⁸ solvothermal (hydrothermal) synthesis⁹⁻¹¹ chemical vapor deposition (CVD)¹² and microwave radiation.¹³

The methods listed above control the size and growth of CdS nanostructure usually by using coating agents, such as surfactants,

ligands, dendrites or polymers to limit the growth in the nanometer structure. Among the diverse methods, the hydrothermal method provides a reasonable way to prepare nanostructures due to its special characteristics such as simplicity, ease of scale up, low-energy consumption and the high purity of the synthesized nanocrystalline materials.¹⁶ In the solvothermal/hydrothermal route, preparation parameters including reaction duration, temperature and solvent type have a significant effect on determining the size and morphology of the products as well as its physical properties.⁸⁻¹⁶ Recently, Yan's group have developed a gentle hydrothermal route to prepare metal sulfides with the use of thioglycolic acids as nontoxic templates.¹⁷ Thus, Peng Zhang and Lian Gao synthesized CdS nanocrystals using carbon disulfide as a sulfurising agent and CTAB (Cetyl trimethylammonium bromide) as a surfactant.¹⁸ A. Phuruangrat et al. successfully synthesized hierarchical tree-like CdS nanostructures with thiourea via a solvothermal method.¹⁹ However, up to now, no report has been presented about cadmium sulfide with Cd(NO₃)₂·4H₂O and thio Schiff-base ligand as a sulfur source. Through the present study, we developed a solvothermal method to synthesize spherical cadmium sulfide nanostructures using propylene glycol as the solvent and a thio Schiff-base as the sulfurising agent without any surfactant for the first time. Different sizes and the influence of preparation parameters such as the nature of solvents, process time, and reaction temperature on crystal structure, size and morphology of cadmium sulfide nanostructures were also investigated.

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Experimental

Materials and physical measurements

All reagents and solvents were of analytical grade and were used as received without further purification. X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Ka radiation. The composition analysis was done by energy dispersive X-ray (EDX, Kevex, Delta Class I). Scanning electron microscopy (SEM) images were obtained on LEO. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu Varian 4300 spectrophotometer using KBr pellets. The electronic spectra of the complexes were taken on a JASCO, (190-2700 nm) with a UV-Visible scanning spectrometer (Model V-670). Thermogravimetric-differential thermal analysis (TG-DTA) was carried out using a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 ml min⁻¹ and a heating rate of 10 °C min⁻¹.

Synthesis of the CdS nanostructures

In a typical procedure, 0.906 g (2.9 \times 10⁻³ mol) of Cd(NO₃)₂. 4H₂O was dissolved in propylene glycol (50 ml) under stirring. In a separate beaker, 0.63 ml (5.88 \times 10⁻³ mol) 2-aminothiophenol (2-ATP) was dissolved in 10 ml absolute ethanol and added drop wise to benzaldehyde solution (0.6 ml benzaldehyde was dissolved in 10 ml absolute ethanol at ambient temperature under magnetic stirring). The two solutions were mixed together and final yellow precipitate solution was transferred to a 70 ml Teflon-line stainless steel autoclave and filled with propylene glycol up to 70% of the total volume. The autoclave was sealed and maintained at 180 °C for 12 h in a digital temperaturecontrolled oven and during the heating period, the solution was neither shaken nor stirred. After thermal treatment, the autoclave was cooled to room temperature and the resulting fulvous precipitate was collected, filtered, washed with distilled water and absolute ethanol several times to remove the unreacted chemicals, and finally dried in a vacuum oven at 60 °C for 5 h. A series of further experiments were carried out to investigate the reaction conditions. The synthetic pathway is shown in Scheme 1.

Results and discussion

In our work, the lowest formation temperature for pure-phase CdS (namely the threshold temperature (TT))²⁰ was firstly checked under hydrothermal conditions. Fig. 1 showed the XRD patterns of the samples synthesized at two different temperatures in the present work. The results indicated that the pure-phase CdS could not be prepared when the reaction was carried out below its TT (160 °C). As shown in Fig. 1a, the product synthesized at 140 °C contained some impurities. As to the CdS samples obtained at the TT of 160 °C for 12 h, the patterns showed that all the diffraction peaks exactly matched the standard pattern (JCPDS Cards, No. 75-0581) of face center cubic structured CdS. These diffraction peaks were indexed to the (111), (200), (220) and (311) diffraction planes of crystalline



Scheme 1 The overall synthetic procedure of the formation of the CdS nanostructures.

CdS (Fig. 1b) and Fig. 1c shows the XRD pattern of the assynthesized CdS at the temperature of 180 °C for 12 h in propylene glycol solvent which the peaks matched with the cubic phase (JCPDS no 75-1545) and hexagonal phase (JCPDS no. 10-0454). The reflection at ~26.8° was well matched to the pure cubic phase and all other peaks perfectly matched those of the pure hexagonal phase. This could be due to the asymmetric rod-like structure present in the sample. Similar results have been observed for the mixed hexagonal and cubic phase of CdS.^{21,22}

The average crystallite size of the nanoparticles was calculated using the Debye–Scherrer formula, $D = 0.94\lambda/\beta \cos \theta$, here λ is the wavelength of the X-ray radiation, D is the crystallite size, β is the line width at half maximum of the corresponding peak and the diffraction angle is θ . The value estimated for the as-synthesized CdS at 160 °C for 12 h in propylene glycol in cubic phase was 9.6 nm.

The initiative of this research compared to other research is that for the synthesis of cadmium sulfide, a new sulfurising agent from the class of thio Schiff-bases was used. This ligand played a complex agent role and sulfurising agent role, and even perhaps a surfactant role without any surfactant or reducing agent needed in the propylene glycol solvent. This solvent plays a significant role in the control of morphology and size of nanoparticles due to it having hydroxyl groups and an appropriate dielectric constant.²⁵ Another advantage of this solvent is that it is cheap, readily available, and environmentally friendly.

Herein, the process could possibly be explained in the following steps: first, the thio Schiff-base (2-(benzylideneamino) benzenethiol) was prepared from benzaldehyde and 2-aminothiophenol. In the second step, the metal salt was dissolved in propylene glycol and interaction occurs between the solvent OH groups and Cd^{2+} . When the former solution was dropped into the latter solution under stirring, interaction



Fig. 1 XRD pattern of the as-synthesized CdS (a) at 140 $^{\circ}$ C for 12 h, (b) at 160 $^{\circ}$ C for 12 h, (c) at 180 $^{\circ}$ C for 12 h in propylene glycol solvent.

occurs between the ligand N and S groups with Cd²⁺ and upon heating the reaction medium up to a sufficiently high temperature, the precursors chemically transform into active atomic or molecular species, forming nanocrystals whose subsequent growth is greatly affected by the presence of ligand and solvent molecules, which could prevent further particle growth and aggregation. Given this probable mechanism, the thio Schiff-base ligand in the hydrothermal system will have been completely consumed and finally CdS produced without any possible impurity phases such as the remaining thio Schiff-base, *S*, *etc.* This is confirmed by the strong and sharp reflection peaks in the XRD pattern which indicate the purity of the spherical CdS nanocrystals. In addition, in the next sections we will see energy-dispersive X-ray analysis (EDX) and Fourier transform infrared FT-IR spectra which further prove the purity of the produced CdS nanocrystals.

Fig. 2(a)–(c) show SEM images of the products produced by the solvothermal method at different temperatures. Keeping other conditions constant revealed that the best temperature is 180 $^{\circ}$ C.



Fig. 2 SEM images of the products with 0.06 M sulfur source in PG for 12 h at (a) 160 $^\circ C$, (b) 180 $^\circ C$, (c) 200 $^\circ C$.

At the temperature of 160 $^{\circ}$ C, nucleation speed is faster than the growth of nanostructures, so the products were composed of a large number of separate particles and were non-uniform. While above this temperature, the small and uniform particles which were obtained at 180 $^{\circ}$ C agglomerated and fused to each other. These results clearly show that the optimum temperature is 180 $^{\circ}$ C. In other experiments at 200 $^{\circ}$ C, growth speed is faster than the nucleation of nanostructures, so the particles obtained were much more fused to each other and their size was smaller.

The SEM images of the as-prepared samples, with different magnification and different reaction times while other conditions remained constant, are presented in Fig. 3(a)-(c). Careful observation of these images suggests that by changing the reaction time from 8 h to 24 h, the structure of the nanoparticles metamorphosed due to the change in nucleation and growth speed of the as-produced CdS. With a reaction time of 8 h, the CdS nuclei were prepared next-door to each other and in this same position grew, and CdS was produced in the



Fig. 3 SEM images of the as-synthesized products at 180 $^\circ C$ for (a) 8 h, (b) 12 h, (c) 24 h.



Fig. 4 SEM images of the as-synthesized products at 180 $^\circ$ C with 0.06 M sulfur source for 12 h in (a) PG, (b) H₂O, and (c) 1-butanol.

hexagonal phase as confirmed by the XRD pattern. While above this time (12 h), nucleation and growth rate is optimal and uniform and separate particles were formed. With the reaction time of 24 h, there was sufficient time for growth in one direction.

Fig. 4(a)-(c) show the as-synthesized CdS in different solvents at 180 °C in hydrothermal processing for 12 h. Nucleation and growth of CdS nanostructures were controlled by the dielectric constant of the solvents. Water has a dielectric constant of 80.1, which is higher than propylene glycol (32.1) and 1-butanol (17.51).²³ In principle, the formation of CdS nanoparticles is attained in a solvent with a high dielectric constant, due to the equilibrium of crystal growth.²⁴ In a low dielectric constant solvent, ion saturation easily occurs, resulting in a high CdS monomer concentration, with a crucial precondition for nonequilibrium of crystal growth. The products in the H₂O system were spherical nanoparticles with a diameter larger than 100 nm (Fig. 4b). In propylene glycol solvent, firstly due to having one hydroxyl group more than 1-butanol and secondly due to it having the dielectric constant above, it may be the specific reaction between the OH groups and the Cd²⁺ ions, which affects the selective growth of various directions of CdS nanocrystals. We speculate that polyols with diverse position and a number of OH groups could play an important role in determining the geometric structures and morphologies of the final products²⁵ (Fig. 4a). Based on the above SEM results, it can be seen that the shape and size of the as-prepared CdS nanocrystals can be affected by reaction time, reaction temperature and solvent type.

To study whether the surface of the as-synthesized CdS was capped with an organic layer the Fourier transform infrared (FT-IR) spectra of the as-synthesized samples were taken. The FT-IR spectrum of the Cd(NO₃) complex with the as-synthesized ligand as well as that of the CdS nanoparticles, prepared at a temperature of 180 °C for 12 h by a simple solvothermal method with solvent of propylene glycol, are shown in Fig. 5(a) and (b) respectively. Absorptions of 3447, 1575, 736, 688 and 481 cm⁻¹ in Fig. 5(a) related to O–H, C—N, C–S, Cd–N



Fig. 5 $\,$ FT-IR spectrum of (a) the Cd(NO₃) complex with the as-synthesized ligand and (b) the CdS nanoparticles as-synthesized at 180 $^\circ$ C for 12 h in PG.

and Cd-S bands respectively, the spectra of CdS nanoparticles show two weak stretch vibrations between 1000 and 2000 cm⁻¹ attributing to the C-H and C=N stretching models of the thio Schiff base and the peak at 561 cm⁻¹ is due to the Cd-S stretching mode.²⁶ In addition, the peak at 3436 cm⁻¹ has been assigned to the ethanol used in the separation step. Indicating thio Schiff base molecules are absorbed on the surface CdS nanoparticles. There was no evidence of free precursor $C_{13}H_{10}NS$, in the sample, because stretch vibration of C–H (ν_{C-H}) and the stretching vibrations of C=N and C=C benzene ring disappeared. Moreover, there is no -HS stretching band at about 2546 cm^{-1} because the Cd^{2+} replaces H^+ in the -HS to form CdS nanoparticles. So the thio Schiff base serves as the complexing ligand that controls growth of CdS nanoparticles. As shown in EDAX analysis, there are no ZnO products in the as-synthesized samples and only ZnS nanoclusters were obtained. The nanocrystal possess good transmittance at 400–4000 cm^{-1} , it indicating that nano-ZnS is a better infraredtransmittance material.

The UV-Vis transmittance spectrum of the CdS nanoparticles is shown in Fig. 6. It reveals that the CdS nanoparticles can absorb the visible light in the range of 500–600 nm. The following equation shows the communication of the absorption coefficient and the incident photon energy of the semiconductor:²⁷

$$\alpha h\nu = K(h\nu - E_{o})^{n}$$

where $h\nu$ is the incident photon energy, *K* is a constant, α is absorption coefficient, $E_{\rm g}$ is the energy gap between the conduction and valance band of the nanoparticles and *n* is 0.5 and 2.0 for a direct transition semiconductor and indirect transition semiconductor, respectively.



Fig. 6 UV-Vis absorption spectra of the as-synthesized CdS at 180 $^\circ C$ for 12 h in PG.



CdS is a direct semiconductor and has a very small absorption coefficient. By drawing the graph of $(\alpha h\nu)^2$ against $h\nu$, the nature of transition involved can be determined. Measurement of the energy gap is achieved through the extrapolation of straight line portions of the plot ($h\nu$ greater than E_g) to the zero absorption coefficients.²⁸ This plot is shown in Fig. 7. A direct band gap value of 2.29 eV was obtained. A typical EDX spectrum of the sample synthesized at 180 °C for 12 h in propylene glycol is shown in Fig. 8, which indicates the



Fig. 8 EDX spectrum of the CdS nanoparticles.



Fig. 9 (a)–(d) TEM images, (e) typical HRTEM image of a single CdS nanocrystal, and (f) their SAED pattern of the CdS nanocrystals synthesized at 180 $^\circ C$ for 12 h.

presence of Cd and S in the product. According to the calculation of the peak areas the molar ratio of the Cd/S is 47.9/52.4, which is very close to the stoichiometric ratio of CdS. Therefore, both XRD and EDX analysis show that pure CdS nanocrystals were successfully produced *via* the present synthetic route.

The size and morphology of the sample synthesized at 180 °C for 12 h in propylene glycol was assessed with transmission electron microscopy (TEM) and selected area diffraction (SAED) pattern measurements. The typical TEM (Fig. 9(a)–(e)) and SAED images (Fig. 9f) of the spherical CdS nanostructures are shown. The TEM image of the CdS shows that the particles have a cubic crystalline phase but strongly overlap together. Also the particles with an average diameter of 12 nm are shown. The SAED pattern of the sample is shown in Fig. 9f and from the center to the edge, it shows diffraction rings of (111), (200), (220), (311), and (222) of the cubic phase. There also exist weak (101) and (102) diffraction rings which belong to the hexagonal crystal phase also indicating which cadmium sulfide nanostructures are polycrystalline with high crystallinity. They are further indexed as the cubic phase. For further approval the structural aspects, the nanoparticles were



Fig. 10 TGA of CdS nanocrystal obtained after removal of the liquid crystal phase by washing with ethanol.

Method	Precursors	Size	Morphology	Ref.
Hydrothermal	$Cd(NO_3)_2$, CS_2 , CTAB	16 nm	Nanoparticle	34
Solvothermal	$Cd(NO_3)_2$, thiourea, en	20 nm in diameter, 100–200 nm in length	Nanowire	35
Solvothermal	$Cd(AC)_2 \cdot 2H_2O$, sulfur powder	114 nm in diameter, 1–2 µm in length	Nanochain	16
			Nanoparticle	
Solvothermal	$Cd(NO_3)_2$, thiourea	40–60 nm in diameter, 1–2 μm in length	Nanoparticle	30
	())		Nanocube	
Hydrothermal	$Cd(AC)_2 \cdot 2H_2O$, ammonium thiocyanate	100–200 nm	Nanorod	31
Hydrothermal	$Cd(AC)_2 \cdot 2H_2O$, S powder, en	26 nm	Nanowire	1
Hydrothermal	$Cd(NO_3)_2$, TGA, PEG	300 nm in diameter, 2–3 μm in length	Nanoparticle	32
Synthesize at ambient temperature	$CdCl_2 \cdot 2H_2O$, TGA	100 nm	Nanoparticle	33
Hydrothermal	$Cd(NO_3)_2$, TGA	25 nm	Nanorod	34
Thermal decomposition	[Bis(salicylaldehydato)cadmium(II)]	10–15 nm	Nanoparticle	35
-	Oleylamine, elemental sulfur		-	

examined by HRTEM. As can be seen from a representative HRTEM image, recorded from one edge of a CdS particle in Fig. 9e. The good lattice fringes show that these nanoparticles are single crystalline and illustrate the correspondence between the crystallite morphology and the crystal orientation.²⁹ The HRTEM image shows sharp lattice margins with 0.28 nm and 0.336 nm spacing, corresponding to the (200) and (111) planes. Therefore, the HRTEM image further verifies the cubic phase nature of the as-synthesized cadmium sulfide nanostructures. Finally there are several cubic cadmium sulfides overlapped together and they create spherical CdS nanostructures that are shown the SEM images.

Thermogravimetry (TG) of CdS is shown in Fig. 10. The TG curve shows that CdS undergoes two weight loss steps. The first weight losses occurs in the temperature range 100–200 $^{\circ}$ C and exhibits 15% weight loss, which corresponds to surface moisture evaporating. The decomposition of the organic template occurred in the temperature range 200–600 $^{\circ}$ C (indicating 76% weight loss). After the sample was heated over 600 $^{\circ}$ C, the sample weight did not change anymore. The small amount of thio Schiff-base molecules in the sample was removed after washing-down to leave only the CdS nanostructures.

In comparison to other similar works, shown in Table 1, our method is more simple and cheaper. In this work, we developed a solvothermal method to synthesize cadmium sulfide in propylene glycol solvent at 180 $^{\circ}$ C for only 12 h with different sizes. The initiative of this research compared to other research is that for the synthesis of cadmium sulfide, a new sulfurising agent from the class of thio Schiff-bases was used. This ligand played either complex agent role and sulfurising agent role and even perhaps a surfactant role without any surfactant or reducing agent needed in the propylene glycol solvent.

The solvent plays a significant role in control of morphology and size of nanoparticles due to having hydroxyl groups and an appropriate dielectric constant. Another advantage of this solvent is that it is cheap, available, and it is environmentally friendly.

Conclusions

The spherical CdS nanostructures were successfully synthesized by a solvothermal method from $Cd(NO_3)_2 \cdot 4H_2O$ using a new sulfurising agent from a class of thio Schiff-base in the presence of propylene glycol as solvent. The effect of some parameters such as, type of solvent and reaction time and temperature on the size and morphology of the obtained products was investigated. The results obtained in the present study show that the solvothermal method has proved to be simple and impressive. The use of toxic chemicals and time-consuming methods was avoided by using the solvothermal method. This method brings forward a broad idea to synthesize other metal sulfides with various morphologies and novel properties.

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